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# SLURRY TREATMENT USING ACIDIFICATION TECHNOLOGY TO REDUCE AMMONIA EMISSION

## UZDATNIANIE GNOJOWICY Z WYKORZYSTANIEM TECHNOLOGII ZAKWASZANIA W CELU ZMNIEJSZENIA EMISJI AMONIAKU

**Summary:** Most of dairy and beef cattle when being grown in barn with a slotted floor is connected with a high concentration of slurry what creates ammonia emission problems. The article presents some proposals for development of new technologies in this area. Using slurry acidification technology in the barn, in the storage or in the field, we can avoid many environmental problems concerning ammonia emission. Besides that, we can save on overall fertilizers' usage in the farm. The ammonia emissions are a major problem associated with animal slurry management, and solutions to overcome this problem are developed worldwide by farmers and scientists. An obvious way to minimize ammonia emissions from slurry is to decrease slurry pH by addition of acids or other substances acting in a similar way. This solution has been used commonly in Denmark, and its efficiency with regard to the minimization of NH<sub>3</sub> emissions has been documented in some studies. Acidification reduced NH<sub>3</sub> emission from stored slurry to less than 10% of the emission from untreated slurry, and the NH<sub>3</sub> emission from the applied slurry on the field was reduced by 67%.

**Keywords:** new technology, slurry acidification technology, ammonia emission, environment protection

**Streszczenie:** Większość bydła mlecznego i mięsnego utrzymywana jest w budynkach inwentarskich wyposażonych w podłogi szczelinowe co powoduje wysoką koncentrację gnojowicy i jest przyczyną emisji dużej ilości amoniaku. W artykule przedstawiono wybrane propozycje dla rozwoju nowoczesnych technologii w tej dziedzinie. Wykorzystanie technologii systemu zakwaszenia gnojowicy w budynkach inwentarskich, zbiornikach lub bezpośrednio na polu pozwala na zmniejszenie emisji amoniaku, co wpływa pozytywnie na ochronę środowiska. Ponadto, możemy zaoszczędzić na ilości nawozów stosowanych w gospodarstwie. Rozwiązaniem tego problemu zajmują się naukowcy, farmerzy na całym świecie. Oczywistym sposobem minimalizacji emisji amoniaku jest zmniejszenie pH gnojowicy poprzez dodawanie kwasów lub innych substancji, działających w podobny sposób. Takie rozwiązania stosowane są w Danii, a jego skuteczność minimalizacji emisji NH<sub>3</sub> zostało udokumentowane w pracach naukowych. Zakwaszenie zmniejsza emisję NH<sub>3</sub> przechowywanej gnojowicy do 10% w porównaniu z gnojowicą bez zakwaszenia, a emisja NH<sub>3</sub> w polu była mniejsza o 67%.

**Słowa kluczowe:** nowe technologie, zakwaszenie gnojowicy, emisja amoniaku, ochrona środowiska

### Introduction

If we take into consideration the problem of slurry influence on country side environment, it is important to provide some analysis of animal production, what has a substantial influence on manure presence in a close distance to houses and flats.

The size of a herd is either expressed in term of head (number of animals) or Livestock Unit (LSU) where one LSU is the grazing equivalent of one adult dairy cow. According to the data of the Polish Ministry of Agriculture on March 2017 there were in Poland 3 732 616 cows at the age of more than 1 year old. When counting beef cattle of the same age there are 1 024 616 animals. Taking into account pigs, there are 11 824 300 animals of these breed. This number included 1 009 700 sows.

Recently more and more livestock barns, in which animals are kept on a slotted floor, instead of manure as organic fertilizer we gain here liquid manure – a mixture of manure, urine and water. The composition and value of natural fertilizer depend on the breeding

technology, feeding and water delivery system. Cow manure and swine manure are different and they show a different effect on the environment. Slurry is usually mixed with some bedding material and some water during management to give the liquid manure with dry matter content in the range from about 1 to 10%. Although potassium is available almost immediately after the application of the manure to the soil, with nitrogen, and especially with phosphorus is not so easy. For phosphorus and a large part of nitrogen, they may be available for plants as nutrients, when a process of mineralization occurs, and generally speaking, must become the activity of soil microflora to provide simple mineral compounds, that can be absorbed by the plant. So the activity of the soil microflora depends on the degree of use of manure as fertilizer [10]. Thus, many studies show that the efficiency of nitrogen supplied in the slurry varies in a very wide range from 30 to 70%. In addition to the mineralization we have to take into account the time – because we want to release the ingredients gradually, along with the course of the growing season. Here, nature favors us, because in the period from April to

the end of August the temperatures are highest, which promotes the development of microflora. To the development of microflora was the most intense, you should provide them with more nutrient components. Slurry as organic fertilizer is used mainly before vegetation. It is important that large doses of manure (especially on light soils) do not precede directly sown plants, as ammonia emitted from the manure can damage and even destroy the root system of rising plants. This assumes that the nutrients and organic matter contained in the slurry should help to increase soil fertility and increase crop yields without the risk of contamination with biogenic compounds of environmental ground water [9].

The use of slurry in an uncontrolled way is a threat to the environment. The European Union legislation allow for the use of natural fertilizers (solid manure, liquid manure, urine) in amount not exceeding 170 kg of nitrogen (N) in pure ingredient per 1 hectare of agricultural land per year [6]. The requirements for agricultural construction sites, utilized for solid manure, slurry and urine storage, are given in the Act of 10 July 2007 concerning fertilizers and fertilization technology. In the case of utilization of liquid manure for many years in doses exceeding the nutritional needs of plants, it can reveal symptoms of the soil fatigue, manifested by the reduced yield of plants. We should, however, take into account the slurry in the fertilization of crops on the farm, as part of the supplementary nutrition. Well-applied manure improves soil physicochemical properties.

The amount of the slurry produced in the EU countries brings all governments to establish special regulations to avoid its harmful influence on the environment in country side surroundings.

### Development of new technology for slurry treatment using concentrated sulfuric acid

The international interest for slurry acidification is quite big and current draft BREF (Reference Document for Best Available Techniques) has recognised slurry acidification, which will become a compulsory to Best Available Technic (BAT) in all EU member states. There are three main technologies, namely in-house, tank and in-field acidification. Their effects in reducing ammonia emissions from stables, stores and fields are substantial, and are found in the range of 40 to 64% according to official tests, among other the Verification Statement (VERA) of technology verification programme set up in cooperation between Danish, German and Dutch environmental authorities [2]. Slurry acidification can be explained as equilibrium between the water bound ammonium ( $\text{NH}_4^+$ ) and the volatile ammonia ( $\text{NH}_3$ ) is moved towards ammonium by adding acid to the slurry. Normally, concentrated sulphuric acid is used, and the costs of the acid in many cases outweighed by savings on purchase of S fertiliser.

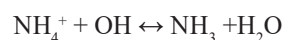
The nitrogen that is captured via avoided ammonia evaporation is turned into savings on purchase of N fertiliser, or in higher crop yields. Slurry acidification also has a considerable climate effect by increasing the carbon sequestration in soil. Reducing the loss of nitrogen from agriculture is a key to reducing eutrophication of the Baltic Sea. Most of the airborne eutrophication to the Baltic Sea comes from ammonia emissions, and in the Baltic State Region

(BSR) almost all ammonia emissions are from livestock manure. Annual deposition of ammonia nitrogen to the Baltic Sea has been increasing during the recent years and it was greater in 2012 than in 1995. While emissions are decreasing slightly in some countries, Baltic Sea Action Plan [4] calls for a reduction of 118,000 tonnes of nitrogen annually to the Baltic Sea, and the Revised Gothenburg Protocol [16] calls for ambitious reductions in ammonia emissions from all Baltic Sea Region (BSR) countries. Slurry acidification also affects solid/liquid slurry separation efficiency positively; DM is higher, N lower and P higher in the solid fraction. A combined treatment should efficiently prevent gaseous emissions, increase fertilizer value of slurry and reduce transport and energy costs.

Acidification of animal slurry has proved to be an efficient solution to minimize  $\text{NH}_3$  emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

Mobile acidification equipment could be suitable for acidifying the slurry in storage during mixing just before spreading. Such equipment could be invested in by the farmer. Mobile equipment implies that the cost can be shared if the same equipment is used on several farms. The service could also be hired from a contractor, under the conditions that there is a contractor in the neighborhood providing this service.

Just to explain, why ammonia evaporation doesn't exists, it can be explained by drawing the following equilibrium in slurry between ammonium salt and ammonia gas



At pH=6.4 all mineralized N is found as ammonium, and no evaporation takes place [4].

In Denmark, the slurry should after lowering the pH<6 be spread within 24 hours according to rules. As the spreading season lasts for longer time, this could mean a period of several weeks per year. Economical calculations are needed to compare which solution is most profitable for individual farms. When hiring the service of acidification, the technology will be available also for smaller farms. Also, if surplus storage volume is needed because of foaming when adding acid, may make the alternative non-profitable compared to the other two alternatives [15].

Orum Smeden's appeared after in field acidification system as much simpler and cheaper. Using this equipment causes a foam formation in the top of the slurry tank, what means that this part of storage capacity is reduced [8]. Such acidification is usually done a few hours or days before spreading on the field, what makes lower ammonia evaporation when spreading such slurry on crops. So far there are about 40 such installations working in Denmark.

In regards to the type of housing, different systems may be used within the same farm. Therefore, livestock within production having more than one type of housing system are counted once for each housing system used on the farm. However, some housing systems only represent a minor share of the actual production [11]. In order to avoid this double counting, the number of places for each type of housing system is used.

For instance, many farms combine different housing system

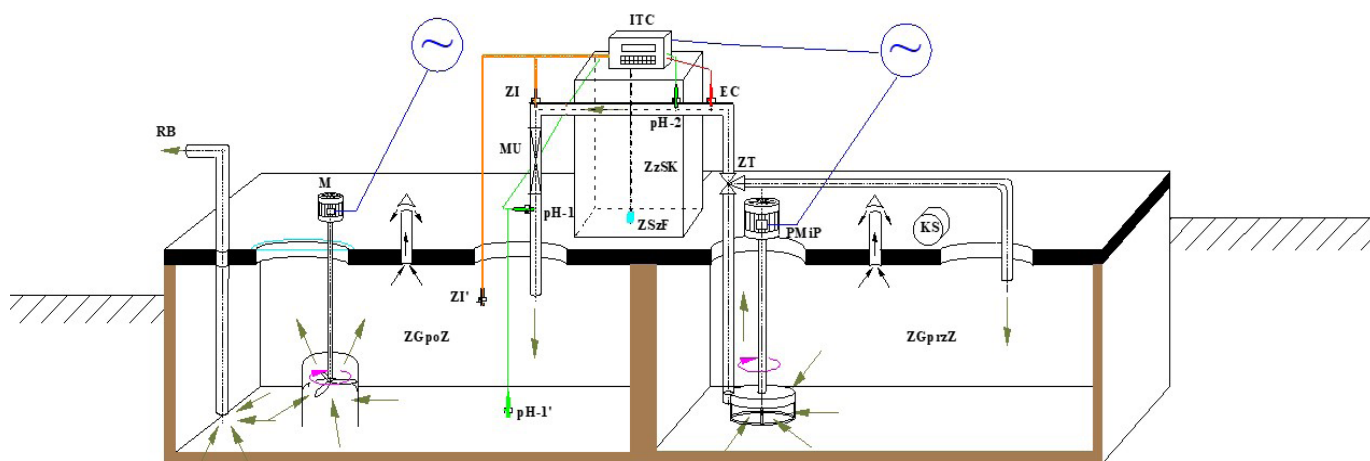


Fig. 1. Experimental pumping of fresh slurry to acidification tank : ITC – dosing pump with pH meter, ZzSK – container with acid, M – mixer, PMiP – pump, ZT – three way valve, ZGprz – tank with fresh slurry, ZGpoz – tank with acidified slurry, RB – discharge pipe

Source: own elaboration

like having slatted floor for the milking cows but solid dung management (deep bed) for the cows about to farrow. Thus, the number of heads on each system changes during the year whereas the number of places is more of an average and represents the actual share of each system [4].

To estimate the potential for each Slurry Acidification Technology (SAT), we should know for each country what are the most represented animal production systems including animal species and what are the most used manure management systems in these most common productions. The manure management systems include the housing types, the storage systems, and the spreading techniques. It is assumed that the SAT is only used for slurry.

The last step of a manure handling system is the spreading stage. There are different techniques for spreading the slurry. Some of them like injection or incorporation have been proven to reduce ammonia emissions [7].

Therefore, Slurry Acidification Technology (SAT) could be seen as an alternative to those techniques. Band-spreading is the technique used in Denmark to apply acidified slurry with as it places the slurry on the soil surface and gives a rather even distribution of the slurry transversal direction.

In the Figure 1, there are presented two slurry tanks, one for fresh slurry and one for acidified slurry. Each one has capacity of 12.5 m<sup>3</sup>. It is the experimental system, but it can be utilized for small family farms as stationary acidification system, where preparing acidified slurry just before spreading it in the field.

System contains: slurry pump, slurry mixer, acid pump, pH meter, nozzle, temperature meter, acid tank, electronic steering unit. Slurry from the barn is coming to the right tank and when it is full, pump provides mixing and pumping all its capacity to the left tank, where the acidification process starts.

When slurry gets a proper pH level, then a tractor with tanker is coming and takes all acidified slurry into the field for spreading, using trailing hoses. This type of experimental system will be very helpful when doing field experimentation on the small plots.

In Figure 2, there are presented the components from electronic system, which provides complete automated work, when providing acidification process. The whole system was elaborated with cooperation of FAPO Co. to provide all experiments in SAT Interreg project on the experimental farm in Falenty near Warsaw.

Normal field acidification tests on a bigger scale will be provided with the help of Orum Semeden's acidified system are presented in Figure 3. This system is quite simple in construction, not much automated units, what can be an advantage, when working in very difficult conditions. This system is very mobile and can be moved from farm to farm and preparing slurry to put acid, than mixing with acid and finally pumping to the tanker and spreading on the field using trailing hoses [13].

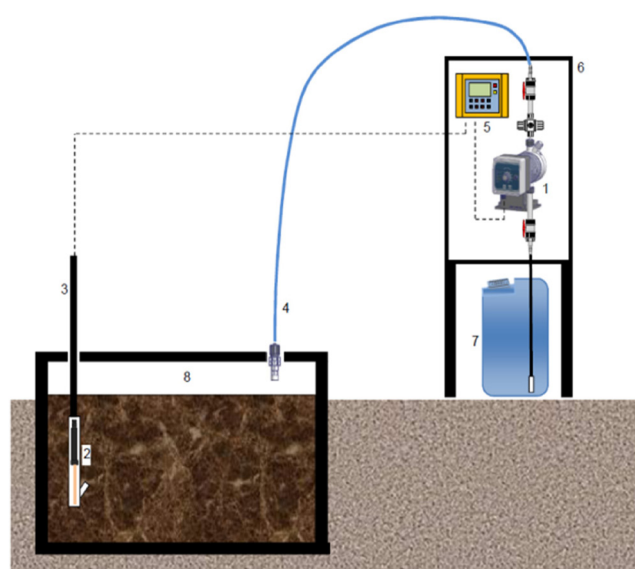


Fig. 2. Fully automated acid delivery system depending on the slurry pH content 1 – acid dosing pump type AMSPLUS, 2 – pH probe type EPHL, 3 – pH probe holder with perfusion system type PECAP-E, 4 – injection line with discharge valve, 5 – control box, 6 – safety cabinet, 7 – container with acid, 8 – slurry tank

Source: FAPO and own elaboration



Fig. 3. Orum Smeden's "in storage" acidification system at work  
Source: Orum Semden's marketing material

Orum Smeden's system [www.oerum-smeden.dk](http://www.oerum-smeden.dk) is based on a slurry mixer, equipped in pipes for adding 98% concentrated sulfuric acid. Slurry is pumped directly in the direction of activity of the mixer, what makes easier to obtain slurry mixture uniformity with acid. This is presented in Figure 3.

Acid pipes are located very close to the slurry mixing screw.

## Results and discussion

Description of processes when adding sulphur acid to slurry is presented below:

$\text{NH}_3$  (ammonia) +  $\text{H}^+$  =  $\text{NH}_4^+$  (ammonium)

$\text{NH}_3$  = gas – may evaporate     $\text{NH}_4^+$  = salt – does not evaporate)

$\text{H}_2\text{SO}_4$  (Sulphur acid) = Hydrogen - Sulphur-Oxygen = Sustainable



Fig.4 Detailed view of acid discharge system of ORUM Co. – construction of "in storage" unit

Source: Orum Semden's marketing material

The concept of reducing slurry pH to get lower nitrogen losses to the air relies on the equilibrium between  $\text{NH}_4$  and  $\text{NH}_3$  what is presented on Figure 5.

The effect of pig and cattle slurry acidification on equivalent of mineral fertilizer is presented in Figure 6.

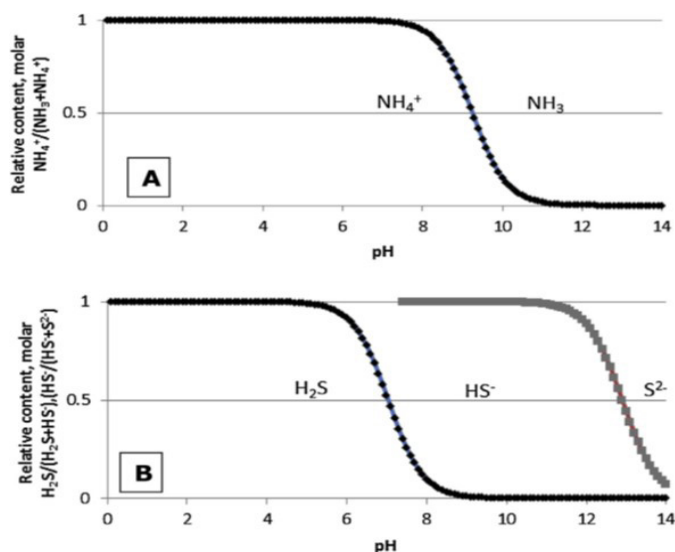


Fig. 5. Effect of slurry pH on its relative content of  $\text{NH}_4^+$  (A) and  $\text{H}_2\text{S}$  (B)[13]

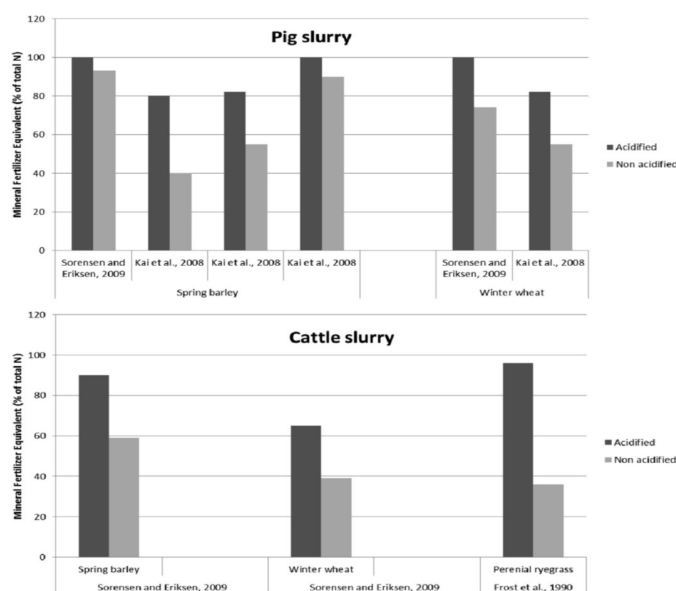


Fig. 6. Effect of pig and cattle slurry acidification on equivalent of mineral fertilizer [4]

There was a strong relationship between  $\text{NH}_3$  emissions and ventilation rate during spring and autumn, but weaker one during the summer period when ventilation rates were generally high. It was concluded that the contribution from floors to  $\text{NH}_3$  emissions was <50%. There was some evidence for reduced  $\text{CH}_4$  emissions from acidified slurry, but  $\text{CH}_4$  emissions were generally low and apparently dominated by enteric fermentation [7]. No effect on  $\text{N}_2\text{O}$  emissions was observed. The effect of acidification on emissions of  $\text{H}_2\text{S}$  differed between the experiments. Implications of slurry acidification on the field state, depends also on N and S availability, and soil pH value [12].

Slurry acidification technology gives many advantages from the point of view of soil fertilization and also the limiting of ammonia emission. Of course, it requires providing safety procedures to avoid a direct contact of farm workers with harmful activity of the acid. But heaving good acidification technology,



which doesn't allow having a direct contact either in the storage area or in the field with the acid, this job is rather safe while fulfilling the procedures.

## Conclusions

- Acidification of animal slurry has proved to be an efficient solution to minimize  $\text{NH}_3$  emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.
- Furthermore, the acidification impacts positively on other slurry treatments such as solid liquid separation or composting; upon the use of a non-sulphur containing additive, it may also impact positively on biogas production. Nevertheless, acidification of slurry might induce higher losses by leaching, due to solubilisation of mineral elements.
- Alternatives to concentrated acids already exist but more research is still needed to improve both their technical and economic aspects. Moreover, the lack of specific equipment for the acidification of solid manures and the separated solid fraction narrows the possible fields of application of the treatment.
- pH level of 5.5- 6.4 is not very acidic, and no more acidic than rain water, which has a normal pH range from 4.5 to 8.5.
- Corrosion of concrete in stables due to use of slurry acidification has never been an issue in Denmark, as it isn't for an outdoor concrete construction like this exposed to rain.
- Acidification reduces  $\text{NH}_3$  emission from pig houses by 70% compared with the standard housing treatment. Little loss was observed from stored slurry, and the  $\text{NH}_3$  emission from the applied slurry was reduced by 67%. In consequence, a 43% (S.E. 27%) increase in mineral fertilizer equivalent (MFE) was measured in the field studies. The slurry acidification system is approved by the Best Available Technology (BAT) in Denmark.

## References

- [1] BalticManure [http://www.balticmanure.eu/en/news/acidification\\_of\\_slurry\\_and\\_biogas\\_can\\_go\\_hand\\_in\\_hand.htm](http://www.balticmanure.eu/en/news/acidification_of_slurry_and_biogas_can_go_hand_in_hand.htm) (accessed 06.05.2014).
- [2] Biocover A/S. (2012). Vera Statement. [http://www.veracert.eu/-/media/DS/Files/Downloads/Artikler/VERA\\_erklaering\\_2012\\_okt\\_enkeltside.pdf](http://www.veracert.eu/-/media/DS/Files/Downloads/Artikler/VERA_erklaering_2012_okt_enkeltside.pdf) (accessed 07.05.2014).
- [3] Fangueiro, D., Surgu, S., Coutinho, J., Vasconcelos, E. (2013). Impact of cattle slurry acidification on carbon and nitrogen dynamics during storage and after soil incorporation. J. Plant Nutr. Soil Sci. 176, 540-550.
- [4] Fangueiro, D., Surgu, S., Napier, V., Menaia, J., Vasconcelos, E., Coutinho, J. (2014). Impact of slurry management strategies on potential leaching of nutrients and pathogens in a sandy soil amended with cattle slurry. J. Environ. Manag. 146, 198-205.
- [4] HELCOM. (2013). Revised nutrient targets. <http://www.helcom.fi/baltic-sea-action-plan/nutrient-reductionscheme/targets> (accessed 06.05.2015).
- [5] Interreg EU - Baltic Sea Region - Baltic Slurry Acidification Project 2016-2019.
- [6] Lyngsø H. F. (2016). Agricultural biogas production in a EU policy context, and ways to enhance effects with slurry acidification technologies. International ITP Conference Monograph, Warsaw, September, 2016.
- [7] Moset, V., Cerisuelo, A., Sutaryo, S., Møller, H.B. (2012). Process performance of anaerobic co-digestion of raw and acidified pig slurry. Water Res. 46, 5019-5027.
- [8] Nørgaard, J.V., Fernandez, J.A., Sørensen, K.U., Wamberg, S., Poulsen, H.D., Kristensen, N.B. (2010). Urine acidification and mineral metabolism in growing pigs fed diets supplemented with dietary methionine and benzoic acid. Livest. Sci. 134, 116-118.
- [9] Nyord, T., Liu, D., Eriksen, J., Adamsen, A.P.S. (2013). Effect of acidification and soil injection of animal slurry on ammonia and odour emission. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.
- [10] Pain, B.F., Misselbrook, T.H., Rees, Y.J. (1994). Effects of nitrification inhibitor and acid addition to cattle slurry on nitrogen losses and herbage. Grass Forage Sci. 49, 209-215.
- [11] Ribeiro, H., Vasconcelos, E., Coutinho, J., Cabral, F. (2009). Treatment by acidification followed by solid-liquid separation affects slurry and slurry fractions composition and their potential of N mineralization. Bioresour. Technol. 100 (20), 4914-4917.
- [12] Roboredo, M., Fangueiro, D., Lage, S., Coutinho, J. (2012). Phosphorus dynamics in soils amended with acidified pig slurry and derived solid fraction. Geoderma 189-190, 328-333.
- [13] Rotz, C.A. (2004). Management to reduce nitrogen losses in animal production. J. Anim. Sci. (Suppl) 82, 119-137.
- [14] Semitela, S., Martins, F., Coutinho, J., Cabral, F., Fangueiro, D. (2013). Ammonia emissions and potential nitrate leaching in soil amended with cattle slurry: effect of slurry pre-treatment by acidification and/or soil application method. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.
- [15] Shi, Y., Parker, D.B., Cole, N.A., Auvermann, B.W., Mehlhorn, J.E. (2001). Surface amendments to minimize ammonia emissions from beef cattle feedlots. Trans.
- [16] UNECE. (2012). Parties to UNECE Air Pollution Convention approve new emission reduction commitments for main air pollutants by 2020 (revised Gothenburg Protocol). <http://www.unece.org/> (accessed 15.05.2014).
- [17] Project implementation contract BIOSTRATEG1/269056/5/NCBR/2015, dated 11.08.2015.

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